THIS PAGE BLANK (USPTO)

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : G03F 7/004

A2

(11) International Publication Number: WO 00/33137

(43) International Publication Date: 8 June 2000 (08.06.00)

(21) International Application Number: PCT/EP99/08391

(22) International Filing Date: 3 November 1999 (03.11.99)

(30) Priority Data:
09/190,763 12 November 1998 (12.11.98) US

(81) Designated States: CN, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
Without international search report and to be republished upon receipt of that report.

(71) Applicant: CLARIANT INTERNATIONAL LTD. [CH/CH]; Rothausstrasse 61, CH-4132 Muttentz (CH).

(72) Inventors: WANAT, Stanley, F.; 3 Frances Lane, Scotch Plains, NJ 07076 (US). RAHMAN, Dalil, M.; 62 Concord Ridge Road, Flemington, NJ 08822 (US). KOKOSZKA, John, J.; 22 Cedar Pond Drive, Apartment 11, Warwick, RI 02886 (US). NARASIMHAN, Balaji; 6A Bartle Court, Highland Park, NJ 08904 (US).

(74) Agent: HÜTTER, Klaus; Clariant GmbH, Patente, Marken, Lizenzen, Am Unisys-Park 1, D-65843 Sulzbach (DE).

(54) Title: PREPARATION OF FRACTIONATED NOVOLAK RESINS BY A NOVEL EXTRACTION TECHNIQUE

(57) Abstract

The present invention provides a method for producing a film forming, fractionated novolak resin having consistent molecular weight and reduced polydispersity, by isolating such novolak resin fractions in a continuous fractionation and separation method using a liquid/liquid centrifuge, thereby reducing processing time and isolation steps which can cause undesirable changes in the novolak resin. A method is also provided for producing photoresist composition from such a fractionated novolak resin and for producing semiconductor devices using such a photoresist composition.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

DESCRIPTION

PREPARATION OF FRACTIONATED NOVOLAK RESINS BY A NOVEL EXTRACTION TECHNIQUE

BACKGROUND OF THE INVENTION

The present invention relates to a process for producing a fractionated film forming novolak resin with good lithographic performance in light sensitive photoresist compositions, and for using such a novolak resin in such light-sensitive compositions. The present invention also relates to a process for fractionating novolak resin by continuous liquid/liquid extraction utilizing a liquid/liquid centrifuge and using such a fractionated resin for making a high quality light-sensitive positive-working photoresist composition. Further, the present invention relates to a process for coating substrates with these light-sensitive compositions, as well as the process of coating, imaging and developing these light-sensitive mixtures on such substrates.

Photoresist compositions are used in microlithography processes for making miniaturized electronic components, such as in the fabrication of computer chips and integrated circuits. Generally, in these processes, a thin coating of a film of a photoresist composition is first applied to a substrate material, such as silicon wafers used for making integrated circuits. The coated substrate is then baked to evaporate any solvent in the photoresist composition and to fix the coating onto the substrate. The baked coated surface of the substrate is next subjected to an image-wise exposure to radiation.

This radiation exposure causes a chemical transformation in the exposed areas of the coated surface. Visible light, ultraviolet (UV) light, electron beam and X-ray radiant energy are radiation types commonly used today in microlithographic processes. After this image-wise exposure, the coated substrate is treated with a developer solution to dissolve and remove either the radiation-exposed or the unexposed areas of the coated surface of the substrate.

Novolak resins are frequently used as the polymeric binder in liquid photoresist formulations. These resins are typically produced by running a

condensation reaction between formaldehyde and one or more multi-substituted phenols, in the presence of an acid catalyst, such as oxalic acid, maleic acid, or maleic anhydride. In producing sophisticated semiconductor devices, it has become increasingly important to provide a film forming novolak resin of superior quality in terms of dissolution rate, better binding properties with a diazonaphthoquinone, and heat resistance.

There are two types of photoresist compositions, negative-working and positive-working. When negative-working photoresist compositions are exposed image-wise to radiation, the areas of the resist composition exposed to the radiation become less soluble to a developer solution (e.g. a cross-linking reaction occurs) while the unexposed areas of the photoresist coating remain relatively soluble to such a solution. Thus, treatment of an exposed negative-working resist with a developer causes removal of the non-exposed areas of the photoresist coating and the creation of a negative image in the coating thereby uncovering a desired portion of the underlying substrate surface on which the photoresist composition was deposited.

On the other hand, when positive-working photoresist compositions are exposed image-wise to radiation, those areas of the photoresist composition exposed to the radiation become more soluble to the developer solution (e.g. a rearrangement reaction occurs) while those areas not exposed remain relatively insoluble to the developer solution. Thus, treatment of an exposed positive-working photoresist with the developer causes removal of the exposed areas of the coating and the creation of a positive image in the photoresist coating. Again, a desired portion of the underlying substrate surface is uncovered.

After this development operation, the now partially unprotected substrate may be treated with a substrate-etchant solution or plasma gases and the like. The etchant solution or plasma gases etch that portion of the substrate where the photoresist coating was removed during development. The areas of the substrate where the photoresist coating still remains are protected and, thus, an etched pattern is created in the substrate material which corresponds to the photomask used for the image-wise exposure of the radiation. Later, the remaining areas of

the photoresist coating may be removed during a stripping operation, leaving a clean etched substrate surface. In some instances, it is desirable to heat treat the remaining photoresist layer, after the development step and before the etching step, to increase its adhesion to the underlying substrate and its resistance to etching solutions.

Positive working photoresist compositions are currently favored over negative working resists because the former generally have better resolution capabilities and pattern transfer characteristics. Photoresist resolution is defined as the smallest feature which the resist composition can transfer from the photomask to the substrate with a high degree of image edge acuity after exposure and development. In many manufacturing applications today, resist resolution on the order of less than one micron are necessary. In addition, it is almost always desirable that the developed photoresist wall profiles be near vertical relative to the substrate. Such demarcations between developed and undeveloped areas of the resist coating translate into accurate pattern transfer of the mask image onto the substrate.

DESCRIPTION OF THE PRIOR ART

In the recent years there has been significant progress in novolak resin synthesis and fractionation. It has been reported that under vigorous synthetic conditions the structure of novolak resin changes, especially when high concentration of acid catalyst and high temperature is used, Rahman et al, "Rearrangement of Novolak Resin", presented at SPIE conference, 1994; Khadim et al "The Nature and Degree of Substitution Patterns in Novolaks by Carbon-13 NMR Spectroscopy", presented at SPIE conference, 1993. In a typical novolak reaction, a reactor is charged with phenolic compounds, an acid catalyst such as oxalic acid, maleic acid, p-toluene sulphonic acid or any mineral acid, and heated to about 95 to 100°C. Formaldehyde is slowly added and the mixture is heated at reflux for about 6 hours. At the end of the condensation period, the reactor is converted to distillation, and the temperature is raised to about 200°C. At this point vacuum is slowly drawn, the temperature is raised to about 220°C, and the

pressure is reduced to below about 20 mm Hg. After the volatiles have been distilled off, the vacuum is released and the molten resin collected and allowed to cool. During the course of the above resin synthesis sequence, samples were taken at various temperatures and inspected by GPC (Gel Permeation Chromatography). It was found that there was a decrease of the weight average molecular weight (all molecular weights are weight average unless otherwise specified) of the polymer, especially in the temperature range between about 160-190°C (Rahman et al, "The Effect of Lewis Bases on the Molecular Weight of Novolak Resins", presented at Ellenville Conference, 1994). The molecular weight decrease (partial depolymerization) was not observed unless the phenolic compounds are extremely pure. If the phenolic compounds contain a trace amount of a Lewis Base, such as a nitrogen base, the molecular weight decrease during the distillation process was not observed. In U.S. Patent No. 5,476,750, assigned to the same assignee as the subject application and incorporated herein by reference, an improved process is disclosed to control molecular weight (avoid substantial depolymerization) by adjusting the amount of Lewis Base in the phenolic compounds before or after the condensation reaction. It was disclosed that during the purification process of such phenolic compounds using an ion exchange resin, distillation, and/or a solvent extraction process, to remove metal ions, the minor amount of Lewis Base present was also removed. Due to the absence of this base, the novolak resin was partially depolymerized during the manufacturing process. The physical properties of the depolymerized resin changed due to degradation, and it was not useful for photoresist compositions. This problem can be substantially avoided by adjusting the level of Lewis Base before or after the condensation step of the novolak resin manufacturing process.

In U.S. Patent No. 5,750,632 (based on patent application Serial No. 366,634, filed on December 30,. 1994), assigned to the same assignee as the subject application and incorporated herein by reference, an improved process is disclosed for isolating a novolak resin at a temperature less than about 140°C by using subsurface forced steam distillation to avoid high temperature molecular weight breakdown of the resin. (Rahman et al, "Isolation of Novolak Resin at Low

Temperature", presented at SPIE Conference, 1996). It is known that a film forming novolak resin can be made by the condensation reaction of a mixture of phenolic monomers with an aldehyde source. Such novolak resin synthesis processes are disclosed in U.S. Patent No. 5,346,799, incorporated herein by reference.

SUMMARY OF THE INVENTION

The present novolak resin fractionation/separation process isolates novolak resin fractions from the phenol formaldehyde condensation product using selective distribution between immiscible liquids in a liquid/liquid centrifuge. The present process is an effective way of continuously or semi-continuously isolating (fractionating and then separating) novolak resin fractions with most of the undesirable lower molecular weight materials removed. It avoids multiple high temperature distillations, which can lead to partial depolymerization of the novolak.

This can be accomplished by dissolving the novolak resin in a water soluble organic polar solvent such as acetone, dimethylformamide (DMF), dimethylsulfoxide (DMS), tetrahydrofuran (THF), ethylene glycol or a C_1–C_5, preferably C_1–C_3, alkyl alcohol, such as ethanol, propanol or preferably methanol, mixed with a typical resist solvent such as propylene glycol methyl ether, propylene glycol methyl ether acetate (PGMEA), 2-heptanone (methyl amyl ketone) or ethyl lactate (EL). This solution comprises the resin layer (A). Another solvent chosen from one or more C_5-C_8 alkanes (such as hexane or heptane), water, or one or more aromatic hydrocarbon solvents such as benzene, toluene, or xylenol or other C_1–C_5 alkyl benzenes, comprises the solvent layer (B).

Solutions (A) and (B) are each fed, either: 1) together as a mixture through one inlet feed, 2) together without being pre-mixed through one inlet feed, or 3) separately through two different inlet feeds, into a liquid/liquid centrifuge (such as one available from CINC, Inc., Carson City, Nevada), where two immiscible liquid layers are initially formed. The heavier or bottom layer contains the high molecular weight (from about 20% to about 100% greater than that of the starting

novolak resin) fraction and the lighter layer contains a mixture of solvents and the lower molecular weight resin fractions (removed from the total distribution of molecular weight) was obtained. The lighter or top layer separates into 2 separate layers, in addition to the heavy layer that has already been formed. However, the force of the revolving centrifuge keeps these 2 distinct layers intermixed until they exit from the centifruge and are allowed to separate. The upper layer of this new lighter 2-layer mixture contains primarily the C_5-C_8 alkane, water or aromatic hydrocarbon solvent with a very small amount of the organic polar solvent and the photoresist solvent, while the lower layer contained higher levels of the organic polar solvent and photoresist solvent, along with about 10-90%, normally 10-30%, by weight of the novolak resin comprised of low molecular weight oligomers (generally in the range of from about 5% to 40% of the molecular weight of the original resin).

The heavier layer or bottom layer and the lighter layer that separates into two phases are each removed from the centrifuge through separate outlets. Either the level of these two outlets may be adjusted or the pressure required to feed liquid through each of the two inlets may be adjusted. By adjusting the inlet feed solutions and maintaining fresh supplies of both the resin in photoresist solvent with organic water soluble solvent and the C_5-C_8 alkane, water or aromatic hydrocarbon solvent, a substantially continuous process is possible.

Subsequent concentration of the heaviest liquid resin layer, such as by distillation of the lower boiling solvents, isolates a fractionated novolak resin solution in the photoresist solvent. This resin solution can then be used directly in the preparation of a photoresist formulation, without the need for more time-consuming isolation steps that could seriously affect the overall molecular weight distribution and polydispersity (Weight Average Molecular Weight/Number Average Molecular weight) of the novolak resin.

The ratio of the resin layer (A) to solvent layer (B) is normally different for each novolak resin system comprised of the 3 types of solvents and the novolak resin, if the molecular weight or molecular weight distribution of the starting material is different. Practical limits for the water soluble organic polar

solvent were dictated by the necessary formation of discreet immiscible layers. For example, the ratio of photoresist solvent, e.g. EL, to organic polar solvent, e.g. MeOH, was from about 10/90 to about 70/30, preferably from about 30/70 to about 60/40, and the ratio of the resin layer (A) solution to the C_5-C_8 alkane, water or aromatic solvent layer (B) is from about 5/1 to about 0.5/1, preferably from about 2/1 to about 1/0.75. These ratios define the most useful ranges where efficient separation occurs.

The typical photoresist solvent utilized in the process of the present invention may comprise propylene glycol methyl ether acetate, 3-methoxy-3-methyl butanol, 2-heptanone (methyl amyl ketone), ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, ethylene glycol monoethyl ether acetate, ethylene glycol monomethyl acetate, methyl ethyl ketone or a monooxymonocarboxylic acid ester, such as methyl oxyacetate, ethyl oxyacetate, butyl oxyacetate, methyl methoxyacetate, ethyl methoxyacetate, butyl methoxyacetate, methyl ethoxyacetate, ethyl ethoxyacetate, ethoxy ethyl propionate, methyl 3-oxypropionate, ethyl 3-oxypropionate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 2-oxypropionate, ethyl 2-oxypropionate, ethyl 2-hydroxypropionate (ethyl lactate), ethyl 3-hydroxypropionate, propyl 2-oxypropionate, methyl 2-ethoxypropionate, or propyl 2-methoxy propionate, or mixtures of one or more of these solvents.

The present invention relates to a process for continuously fractionating and separating a film forming novolak resin. The final fractionated and separated novolak resin is dissolved in one essentially pure photoresist solvent, and is substantially free from lower molecular weight isomers and unreacted starting materials. In addition, the isolated novolak resin solution can then be easily used without the need for additional time consuming and costly isolation steps. The novolak resin solution useful for formulation into photoresist formulations can be completed by removing the small amounts of lower boiling solvents present, such as by simply distilling off, until the solvent remaining is substantially the pure photoresist solvent of choice. Additional isolation steps that were commonly needed have been shown to cause rearrangement and unacceptable increases in

overall resin polydispersity. The resins of the present invention show good lithographic performance in light-sensitive photoresist compositions. The invention also relates to a process for producing such a photoresist composition containing such a novolak resin. The invention further relates to a process for producing semiconductor devices using such photoresists containing such a novolak resin, photoresist solvent(s), and a photosensitizer.

Film forming novolak resins having substantially consistent molecular weight (no substantial depolymerization) and relatively low polydispersity lend themselves to superior lithographic performance when incorporated into photoresist compositions. The resins themselves may be obtained by condensing a formaldehyde with one or more phenolic compounds, such as m-cresol, p-cresol, 2,4- and 2,5-dimethylphenol, 3,5-dimethylphenol, 2,3,5-trimethylphenol, or mixtures thereof. The condensation reaction is preferably carried out in the presence of an acid catalyst, such as oxalic acid, maleic acid, maleic anhydride, p-toluene-sulphonic acid or sulfuric acid.

The present invention provides a process for producing a film forming novolak resin, which process comprises:

a) condensing (reacting) formaldehyde, para formaldehyde or formalin with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin;

b) adding a water soluble organic polar solvent and a photoresist solvent, such as propylene glycol methyl ether acetate, 2-heptanone or ethyl lactate, to the novolak resin reaction mixture from step a), at a ratio of photoresist solvent to water soluble organic polar solvent of from about 10/90 to 70/30, preferably from about 30/70 to 60/40;

c) feeding the mixture from step b) into a liquid/liquid centrifuge at a feed rate of from about 0.01 to 100 gallons per minute (gal./min.) and at a temperature of from about 0°C up to a maximum temperature that is less than the boiling point of the lower boiling solvent in the mixture from step b), preferably up to about 10°C less than said boiling point, most preferably up to about 20°C less than said boiling point, and feeding a

substantially pure C_5–C_8 alkane, water or aromatic hydrocarbon solvent into a separate liquid/liquid centrifuge inlet port at a feed rate of from about 0.01 to 100 gal./min., at a ratio of water soluble organic polar solvent/photoresist solvent from step b) to C_5–C_8 alkane, water or aromatic solvent, of from about 5:1 to about 0.5:1, preferably from about 2:1 to about 1:0.75;

d) rotating the liquid/liquid centrifuge containing the mixture from step c) at an rpm (revolutions per minute) of at least 500 rpm, preferably from about 500 to about 50,000 rpm, most preferably from about 1,000 to about 30,000 rpm, and thereby separating and collecting a two-phase system, from 2 separate outlet ports into two containers, wherein the heavier phase (H) contains the higher molecular weight novolak resin fraction, in the water soluble organic polar solvent and the photoresist solvent with a minor amount (less than 5% by weight) of the C_5–C_8 alkane, water or aromatic hydrocarbon solvent, and the lighter phase (L) contains: 1) the lower molecular weight novolak resin fraction, 2) C_5–C_8 alkane, water or aromatic hydrocarbon solvent, 3) water soluble organic polar solvent, and 4) photoresist solvent;

e) as the lighter phase (L) of the two-phase system of step d) is collected it may separate into two phases, the lighter of these two second phases containing the C_5–C_8 alkane, water or the aromatic hydrocarbon solvent and a minor amount (less than 5% by weight) of the water soluble organic polar solvent and about 15-20% of the photoresist solvent, the heavier of these two second phases containing low molecular weight novolak oligomers and unreacted phenolic compounds, dissolved in the water soluble organic polar solvent and the photoresist solvent with about 10-15% of the C_5-C_8 alkane, water or aromatic hydrocarbon;

f) substantially removing the residual C_5-C_8, water or aromatic hydrocarbon solvent from the heavier phase (H) from step d), such as distilling the heavier phase (H), and leaving the novolak resin in the photoresist solvent. The resin solution may then be used upon demand for the preparation of

photoresists. The distillation is carried out at a temperature below the boiling point of the photoresist solvent, preferably at a temperature of from about 40°C. to about 100°C., at a pressure from about 20 mm of mercury to about 760 mm of mercury for from about 10 minutes to about 30 minutes; and, optionally;

g) adding additional photoresist solvent and continuing distillation until the desired concentration of the novolak resin in substantially pure photoresist solvent is obtained.

The present invention further provides a process for producing a positive photoresist composition having superior lithographic performance. The subject process comprises: providing an admixture of: 1) a photosensitive component in an amount sufficient to photosensitize a photoresist composition; 2) the film forming novolak resin solution produced by the above-described process of the present invention and 3) additional photoresist solvent, as needed to produce the desired formulation, and thereby forming a light-sensitive photoresist composition.

The invention further provides a method for producing a semiconductor device by producing a photo-image on a substrate by coating a suitable substrate with a positive working photoresist composition. The subject process comprises:

a) coating a suitable substrate with a photoresist composition produced by the above-described process containing a novolak resin produced by the above-described process of the present invention;

b) heat treating the coated substrate of step a) until substantially all of the photoresist solvent is removed; image-wise exposing the photosensitive composition and removing the image-wise exposed areas of such composition with a suitable developer, such as an aqueous alkaline developer. Optionally one may also perform a baking of the substrate either immediately before or after the removing step.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Novolak resins have been commonly used in the art of photoresist manufacture as exemplified by "Chemistry and Application of Phenolic Resins", Knop A. And Scheib, W.; Springer Verlag, New York, 1979 in Chapter 4. Similarly, o-quinone diazides are well known to the skilled artisan as demonstrated by "Light Sensitive Systems", Kosar, J.; John Wiley & Sons, New York, 1965 Chapter 7.4. However, the instant invention has found that the use of particular resins isolated by separation of fractionated resins in the heaviest layer of a 2 or 3 layer separation, using a high shear liquid/liquid centrifuge, provides comparable or better lithographic performance at a fraction of the time required with traditional isolation processes. The instant invention shows that using such a semi-continuous fractionation and separation, useful novolak resins can be made for photoresists.

Optional ingredients for the photoresist compositions of the present invention include colorants, dyes, anti-striation agents, leveling agents, plasticizers, adhesion promoters, speed enhancers, solvents and such surfactants as non-ionic surfactants, which may be added to the solution of novolak resin, sensitizer and solvent before the photoresist composition is coated onto a substrate. Examples of dye additives that may be used together with the photoresist compositions of the present invention include Methyl Violet 2B (C.I. No. 42535), Crystal Violet (C.I. 42555). Malachite Green (C.I. No. 42000), Victoria Blue B (C.I. No. 44045) and Neutral Red (C.I. No. 50040) at one to ten percent weight levels, based on the combined weight of novolak and sensitizer. The dye additives help provide increased resolution by inhibiting back scattering of light off the substrate.

Anti-striation agents may be used at up to about a five percent weight level, based on the combined weight of novolak and sensitizer. Plasticizers which may be used include, for example, phosphoric acid tri-(beta-chloroethyl)-ester; stearic acid; dicamphor; polypropylene; acetal resins; phenoxy resins; and alkyl resins, at about one to ten percent weight levels, based on the combined weight of novolak and sensitizer. The plasticizer additives improve the coating properties of

the material and enable the application of a film that is smooth and of uniform thickness to the substrate.

Adhesion promoters which may be used include, for example, beta-(3,4-epoxy-cyclohexyl)-ethyltrimethoxysilane; p-methyl-disilane-methyl methacrylate; vinyl trichlorosilane; and gamma-amino-propyl triethoxysilane, up to about a 4 percent weight level, based on the combined weight of novolak and sensitizer. Development speed enhancers that may be used include, for example, picric acid, nicotinic acid or nitrocinnamic acid up to about a 20 percent weight level, based on the combined weight of novolak and sensitizer. These enhancers tend to increase the solubility of the photoresist coating in both the exposed and unexposed areas, and thus they are used in applications when speed of development is the overriding consideration even though some degree of contrast may be sacrificed; i.e., while the exposed areas of the photoresist coating will be dissolved more quickly by the developer, the speed enhances will also cause a larger loss of photoresist coating from the unexposed areas.

The solvents may be present in the overall composition in an amount of up to 95% by weight of the solids in the composition. Solvents, of course are substantially removed after coating of the photoresist solution on a substrate and subsequent drying. Non-ionic surfactants that may be used include, for example, nonylphenoxy poly(ethyleneoxy) ethanol; octylphenoxy ethanol at up to about 10% weight levels, based on the combined weight of novolak and sensitizer.

The prepared photoresist solution, can be applied to a substrate by any conventional method used in the photoresist art, including dipping, spraying, whirling and spin coating. When spin coating, for example, the resist solution can be adjusted with respect to the percentage of solids content, in order to provide coating of the desired thickness, given the type of spinning equipment utilized and the amount of time allowed for the spinning process. Suitable substrates include silicon, aluminum, polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polysilicon, ceramics, aluminum/copper mixtures; gallium arsenide and other such Group III/V compounds.

The photoresist coatings produced by the described procedure are particularly suitable for application to thermally grown silicon/silicon dioxide-coated wafers, such as are utilized in the production of microprocessors and other miniaturized integrated circuit components. An aluminum/aluminum oxide wafer can also be used. The substrate may also comprise various polymeric resins, especially transparent polymers such as polyesters. The substrate may have an adhesion promoted layer of a suitable composition, such as one containing hexa-alkyl disilazane, preferably hexamethyl disilazane (HMDS).

The photoresist composition solution is then coated onto the substrate, and the substrate is treated at a temperature from about 70°C to about 110°C for from about 30 seconds to about 180 seconds on a hot plate or for from about 15 to about 90 minutes in a convection oven. This temperature treatment is selected in order to reduce the concentration of residual solvents in the photoresist, while not causing substantial thermal degradation of the photosensitizer. In general, one desires to minimize the concentration of solvents and this first temperature treatment is conducted until substantially all of the solvents have evaporated and a thin coating of photoresist composition, on the order of one micron in thickness, remains on the substrate. In a preferred embodiment the temperature is from about 85°C to about 95°C. The treatment is conducted until the rate of change of solvent removal becomes relatively insignificant. The temperature and time selection depends on the photoresist properties desired by the user, as well as the equipment used and commercially desired coating times. The coated substrate can then be exposed to actinic radiation, e.g., ultraviolet radiation, at a wavelength of from about 300 nm to about 450 nm, x-ray, electron beam, ion beam or laser radiation, in any desired pattern, produced by use of suitable masks, negatives, stencils, templates, etc.

The photoresist is then optionally subjected to a post exposure second baking or heat treatment, either before or after development. The heating temperatures may range from about 90°C to about 120°C, more preferably from about 100°C to about 110°C. The heating may be conducted for from about 30

seconds to about 2 minutes, more preferably from about 60 seconds to about 90 seconds on a hot plate or about 30 to about 45 minutes by convection oven.

The exposed photoresist-coated substrates are developed to remove the image-wise exposed areas by immersion in an alkaline developing solution or developed by a spray development process. The solution is preferably agitated, for example, by nitrogen burst agitation. The substrates are allowed to remain in the developer until all, or substantially all, of the photoresist coating has dissolved from the exposed areas. Developers may include aqueous solutions of ammonium or alkali metal hydroxides. One preferred hydroxide is tetramethyl ammonium hydroxide. After removal of the coated wafers from the developing solution, one may conduct an optional post-development heat treatment or bake to increase the coating's adhesion and chemical resistance to etching solutions and other substances. The post-development heat treatment can comprise the oven baking of the coating and substrate below the coating's softening point. In industrial applications, particularly in the manufacture of microcircuitry units on silicon/silicon dioxide-type substrates, the developed substrates may be treated with a buffered, hydrofluoric acid base etching solution. The photoresist compositions of the present invention are resistant to acid-base etching solutions and provide effective protection for the unexposed photoresist-coating areas of the substrate.

The following specific examples will provide detailed illustrations of the methods of producing and utilizing compositions of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention. Unless otherwise specified, all parts and percents are by weight, all temperatures are in degrees Centigrade, and all molecular weights are weight average molecular weight.

Example 1

Novolak resin A was synthesized by condensing formaldehyde with a mixture of 55% meta-cresol and 45% para-cresol at a ratio of 0.7 mole of formaldehyde to 1 mole of total cresols (meta cresol plus para cresol). The reaction was run with oxalic acid catalyst. After reacting the mixture for about 6 hrs. at about 90-95°C, the mixture was distilled at a temperature up to about 200°C, and then at 200°C with 25-30 mm Hg vacuum, to substantially remove unreacted cresols. The molten novolak resin was poured into a crystallizing dish and allowed to cool. The solidified resin was broken up and powdered by grinding the resin with a mortar and pestle.

Example 2

Novolak resin, produced according to the procedure of example 1, was dissolved in PGMEA to make a 30% solids solution. This novolak resin solution was diluted to 20% solids by adding MeOH, so that the final solvent composition was 58% PGMEA and 42% MeOH. This solution was used as one of two inlet feed streams for a CINC™ model V2 liquid/liquid centrifuge. The other inlet feed stream was hexane. The pump speeds for each inlet stream had separate controls. Trials were run with a range of temperatures from 0-55°C, centifruge rotor rpm of from 1500-5000 (equating to g forces between 100 and 800, respectively) and inlet feed ratios (and corresponding outlet feed ratios) of from about 3 parts of the novolak resin solution to about 0.5 parts of the C_5-C_8 alkane or aromatic hydrocarbon to about 0.5 parts of the novolak resin solution to about 2 parts of the C_5-C_8 alkane or hydrocarbon solvent. Acceptable ranges varied for each polymer and were dictated by having an observable separation into distinct, immiscible phases. A screening design showed that the feed ratio and temperature also had an effect on the Mw (weight average molecular weight) and DR (dissolution rate) of the final fractionated and separated novolak resin. Table I below shows the conditions used, the Mw determined by GPC and the DR for the final product. The experiments, the results of which are set forth in Table I below, demonstrated

that the present method effectively fractionated and separated a novolak resin in a process that lends itself to a continuous or semi-continuous mode.

Comparative DRs were run in AZ® 300 MIF tetramethyl ammonium hydroxide developer (available from AZ Electronic Materials, Clariant Corporation, Somerville, NJ) comparing a sample of unfractionated novolak resin dissolved in PGMEA to the novolak resin solution obtained from the heaviest phase of the 3-phase separation. The DR measurement was run on a Xinix™ Model 2200 Process Monitor. Silicon wafers, primed with hexamethyldisilizane (HMDS), were coated with 28% solids novolak resin solution at 110°C. for 60 seconds at a spin speed appropriate to give a coated film thickness of 1.60 ± 0.1 micrometers, as measured on a Nano™ 215 device using the 5 point 4-inch wafer program. A wafer was attached to the Xinix™ probe and was immersed in a bath of AZ® 300 MIF developer until the resin was removed. Two wafers were run and averaged to obtain the DR as measured in Angstroms/ second (Å/sec.). Whereas the unfractionated resin had a DR of about 200 Å/sec., the fractionated material had a DR of about 60 Å/sec to 90 Å/sec. Weight average molecular weights (Mw) measured by gel permeation chromatography (GPC) showed that the fractionated resin had a Mw of about 9,500-12,000 whereas the unfractionated resin had a Mw of about 7,500.

Table I

Trial	Temp., °C	rpm	R/H	Mw, GPC	PD, Mw/Mn	DR, Å/sec.
1	55	1000	2	9917	5.1	-----------
2	0	5000	1	9941	5.4	-----------
3	0	1000	2	9046	5.1	-----------
4	55	1000	0.5	11710	5.0	69.5
5	55	5000	2	9601	5.0	-----------
6	25	3500	2	9536	5.1	-----------
7	25	1000	1	10069	5.0	-----------
8	55	3500	1	10002	5.0	-----------
9	0	1000	0.5	8788	5.3	-----------
10	25	5000	0.5	9846	5.1	-----------
11	25	5000	2	10274	5.3	-----------
12	0	3500	2	10115	5.8	-----------
13	0	3500	0.5	9513	5.4	-----------
14	55	5000	1	12544	6.0	95.3
15	0	1000	1	9803	5.4	-----------

An unfractionated control sample had a Mw of about 7500 and a DR of about 200 Å/sec. with polydispersities of about 15.

R= pump speed to the inlet feed of a 20% solids novolak resin solution in 58% PGMEA/42% MeOH

H= pump speed to the inlet feed of n-hexane

PD = Polydispersity = Mw/Mn

Example 3

Another series of experiments was run according to the procedure of Example 2, where the temperature was held constant at 55°C and the centrifuge rpm was maintained at 3500 rpm (~500 g force). In this series, the only variable was the composition of the novolak resin solution and the solvent where ethyl lactate (EL) was used as the photoresist solvent in place of PGMEA. The EL/MeOH ratio was held at 58/42%. Dissolution Rates (DR) ranging between about 30 and 190 Å/sec. were obtained as compared to unfractionated resins that had a dissolution rate of about 300 Å/sec. The results are shown in Table II below.

Table II

Trial	Temp.,°C	R/H	Mw, GPC	PD	DR, Å/sec.
1	55	2	11,247	8.8	137.9
2	40	2	11,481	9.2	146.3
3	35	0.5	10,169	8.6	145.6
4	25	0.5	11,368	9.5	187.3
5	40	2	11,728	9.3	149.6
6	25	2	11,857	9.6	176.5
7	55	2	11,340	4.3	140
8	25	2	11,674	9.4	186.7
9	55	0.5	14,155	8.1	40.6
10	55	1	12,659	9.7	159.2
11	25	1.25	11,980	9.6	189.9
12	25	1.25	11,183	9.1	191.2
13	55	1.5	12,032	9.3	113.4
14	35	1.5	11,688	9.4	143.4
15	45	0.5	10,999	9.0	127.4
16	55	0.5	13,862	6.8	28.5

An unfractionated control sample had a Mw of about 9000, a DR of about 300 Å/sec and a PD of about 15.

R= pump speed to the inlet feed of a 20% solids novolak resin solution in 58% EL/42% MeOH

H= pump speed to the inlet feed of n-hexane.

Example 4

A novolak resin was synthesized by condensing para formaldehyde with a mixture of 5 moles of meta-cresol, 4 moles of para-cresol, and 2 moles of 2,3,5-trimethyl phenol at a ratio of about 0.7 moles of formaldehyde to 1 mole of total

phenols. The reaction was run with oxalic acid catalyst. After reacting the mixture for about 4 hrs. at about 90-95°C, the mixture was distilled up to about 200°C and then at 200°C with 25-30 mm Hg vacuum to remove unreacted cresols. The molten resin was poured into a crystallizing dish and allowed to cool. The solidified resin was broken up and powdered by grinding the resin with a mortar and pestle.

A 20% solids solution of the above novolak resin was made by dissolving 270 grams of the solid novolak resin in 875.5 grams of MeOH and 229.1 grams of EL. This solvent composition was 79.3% MeOH and 20.7% EL. To this solution, 341.5 grams of deionized water was added and the mixture was fed through one inlet, at a rate of 200 milliliters (ml.) per minute at room temperature, into a CINC™ model V-2 liquid/liquid centrifuge running at 4000 rpm (~600 g force). The mixture was efficiently separated into two distinct layers, the heavy layer containing one phase and the lighter layer containing two other phases, which are in a mixture. The lighter layer and the heavy layer were removed from the centrifuge through two separate outlet feeds, each at a rate of about 200 ml./min. The heavy layer was collected, and water was removed by vacuum distillation until the final solution was 30% solids in pure EL.

Comparative dissolution rates (DR) were run in AZ® 300 MIF developer by the method described in example 2. A sample of unfractionated resin dissolved in ethyl lactate solution was compared to the resin obtained from the heavier phase of the phase separation. Whereas the unfractionated resin had a DR of 800 Å/sec., the fractionated material had a DR of 60 Å/sec. Molecular weights (Mw) by gel permeation chromatography (GPC) showed that the fractionated resin had an Mw of 5147 whereas the unfractionated resin had a Mw of 2104.

Example 5

A 50 gram photoresist test sample was prepared for testing fractionated resin from example 4 according to the following formulation:

NK-280 (a proprietary 2,1,5- diazonaphthoquinone sulfonyl chloride based sensitizer from Nippon Zeon Co)	2.02 gm
NK-240 (a proprietary 2,1,4-diazonaphthoquinone sulfonyl chloride based sensitizer from Nippon Zeon Co.)	0.84 gm
Fractionated novolak Resin (lot# 68020, 30% solids in EL from Hoechst Celanese Corp.)	22.58 gm
B126X-SH porprietary speed enhancer resin available from Nippon Zeon Co.	1.20 gm
KP-341, a striation free surfactant from Shinetsu Chem. Co. (2% in Ethyl Lactate)	0.004 gm
Additional ethyl acetate added	17.15 gm
n-Butyl Acetate	5.85 gm

The photoresist resist sample was coated on an HMDS primed silicon wafer to a 1.083 micrometer (μm) film thickness, and was soft baked at 90°C for 60 seconds on a hot plate. The focus exposure matrix was printed on the coated wafers using a 0.54 NA NIKON® i-line stepper and a NIKON® resolution reticle. The exposed wafers were PEB (post exposure baked) at 110°C for 70 seconds on an in-line hot plate. The wafers were then developed using AZ® 300 MIF (TMAH, tetramethyl ammonium hydroxide - 2.38%) developer for 60 seconds at 21°C. The developed wafers were examined using a HITACHI® S-4000 SEM (scanning electron microscope). A nominal dose (Dose to Print, DTP) was measured at the best focus by choosing the exposure at which the printed feature most closely matched the mask feature size on the developed SEM photo. For this resist, the dose required to precisely replicate a given feature was 290

millijoules/cm^2. Resolution is the minimum feature size which can be discriminated (resolved) and was judged to be 0.32 μm. Depth of focus depth of focus is the range of usable focus at which nominal sizes can still be resolved. The depth of focus for the test resist was 1.0 μm.

Example 6

A novolak resin was synthesized by condensing para formaldehyde with a mixture of 5 moles of meta-cresol, 4 moles of para-cresol, and 2 moles of 2,3,5-trimethyl phenol at a ratio of about 0.7 moles of formaldehyde to 1 mole of total phenols . The reaction was run with oxalic acid catalyst. After reacting the mixture for about 4 hrs. at about 90-95°C, the mixture was distilled up to about 200°C and then at 200°C with 25-30 mm Hg vacuum to remove unreacted cresols. The molten resin was poured into a crystallizing dish and allowed to cool. The solidified resin was broken up and powdered by grinding the resin with a mortar and pestle.

A 30% solids solution of the resin was made by dissolving 240 grams of resin in 560 grams of ethyl lactate (EL). This solution was diluted to 20% solids by the addition of methanol (MeOH) such that the final solvent ratio was 58% EL to 42% MeOH. This solution was used as one inlet feed stream (R) with hexane as the other feed stream (H) using conditions similar to those found in example 2. The R/H ratio was maintained at 1/1 by running the respective feed pumps at the same rate (~ 4 kgs./minute), the temperature was 40°C and the centrifuge spin speed was 3500 rpm. The heavy layer was distilled to remove residual MeOH and hexane and was concentrated to 26% solids. The dissolution rate (DR) was measured according to the procedure described in example 2. The fractionated resin of this example had a DR of about 270 Å/sec. while the unfractionated resin had a DR of about 600 Å/sec.

Comparative dissolution rates (DR) were run in AZ® 300 MIF developer by the method described in example 2. A sample of unfractionated resin dissolved in ethyl lactate solution was compared to the resin obtained from the heavier phase of the phase separation. Whereas the unfractionated resin had a DR of 800 Å/sec.,

the fractionated material had a DR of 60 Å/sec. Molecular weights (Mw) by gel permeation chromatography (GPC) showed that the fractionated resin had an Mw of 6365 whereas the unfractionated resin had a Mw of 2860.

WHAT WE DESIRE TO CLAIM IS:

1. A method for producing a film forming novolak resin which comprises:

a) condensing formaldehyde, para formaldehyde or formalin with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin;

b) adding a water soluble organic polar solvent and a photoresist solvent to the novolak resin reaction mixture from step a), at a ratio of photoresist solvent to water soluble organic polar solvent of from about 10/90 to 70/30;

c) feeding the mixture from step b) into a liquid/liquid centrifuge at a feed rate of from about 0.01 to 100 gallons per minute and at a temperature of from about 0°C up to a maximum temperature that is less than the boiling point of the lower boiling solvent in the mixture from step b) and feeding a substantially pure C_5–C_8 alkane, water or aromatic hydrocarbon solvent into a separate liquid/liquid centrifuge inlet port through an inlet feed at a feed rate of from about 0.01 to 100 gal./min., at a ratio of water soluble organic polar solvent/photoresist solvent from step b) to C_5–C_8 alkane, water or aromatic solvent, of from about 5:1 to about 0.5:1;

d) rotating the liquid/liquid centrifuge containing the mixtures from step c) at a speed of at least 500 rpm and thereby separating and collecting a two-phase system from 2 separate outlet ports, into two containers, wherein the heavier phase (H) contains the higher molecular weight novolak resin fraction, in the water soluble organic polar solvent and the photoresist solvent with a minor amount of the C_5–C_8 alkane, water or aromatic hydrocarbon solvent, and the lighter phase (L) contains: 1) the lower molecular weight novolak resin fraction, 2) C_5–C_8 alkane, water or aromatic hydrocarbon solvent, 3) water soluble organic polar solvent, and 4) photoresist solvent;

e) as the lighter phase (L) of the two-phase system of step d) is collected, it may separate into two phases, the lighter of these two second phases

containing the C_5–C_8 alkane, water or the aromatic hydrocarbon solvent and a minor amount of the water soluble organic polar solvent and about 15-20% of the photoresist solvent, the heavier of these two second phases containing low molecular weight novolak oligomers and unreacted phenolic compounds, dissolved in the water soluble organic polar solvent and the photoresist solvent with about 10-15% of the C_5-C_8 alkane, water or aromatic hydrocarbon;

f) substantially removing the residual C_5-C_8, water or aromatic hydrocarbon solvent from the heavier phase from step d) and leaving the novolak resin dissolved in the photoresist solvent.

2. The method of claim 1 wherein said acid catalyst is oxalic acid, maleic acid, maleic anhydride, sulfuric acid or p-toluene sulphonic acid.

3. The method of claim 1 wherein the water soluble organic polar solvent added in step b) is acetone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, ethylene glycol or a C_1-C_5 alkyl alcohol.

4. The method of claim 1 wherein the photoresist solvent added in step b) is a monooxymonocarboxylic acid ester, a propylene glycol methyl ether acetate, 2-heptanone or a propylene glycol methyl ether, or a mixture of one or more of these.

5. The method claim 1 wherein aromatic hydrocarbon solvent added in step b) is benzene or a C_1–C_5 alkyl benzene.

6. The method of claim 1 wherein the ratio of photoresist solvent to water soluble organic polar solvent added in step b) is from about 10/90 to 70/30.

7. The method of claim 1 wherein the ratio of photoresist solvent to water soluble organic polar solvent added in step b) is from about 30/70 to 60/40.

8. The method of claim 1 wherein the ratio of the mixture from step b) fed into the centifruge to the C_5–C_8 alkane, water or aromatic hydrocarbon solvent fed into the centifruge is from about 2:1 to about 1:0.75.

9. The method of claim 1 wherein in step b) the materials are fed into the centrifuge at a temperature of from about 0°C to a temperature up to about 10°C less than the boiling point of the lower boiling solvent.

10. The method of claim 1 wherein the centifruge is rotated at a speed of from about 500 to 50,000 rpm.

11. The method of claim 1 wherein the centifruge is rotated at a speed of from about 1,000 to 30,000 rpm.

12. A method for producing a positive photoresist composition using the resin solution of the instant invention comprising:

a) condensing formaldehyde, para formaldehyde or formalin with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin;

b) adding a water soluble organic polar solvent and a photoresist solvent to the novolak resin reaction mixture from step a), at a ratio of photoresist solvent to water soluble organic polar solvent of from about 10/90 to 70/30;

c) feeding the mixture from step b) into a liquid/liquid centrifuge at a feed rate of from about 0.01 to 100 gallons per minute and at a temperature of from about 0°C up to a maximum temperature that is less than the boiling point of the lower boiling solvent in the mixture from step b) and feeding a substantially pure C_5–C_8 alkane, water or aromatic hydrocarbon solvent into a separate liquid/liquid centrifuge inlet port at a feed rate of from about 0.01 to 100 gal./min., at a ratio of water soluble organic polar

solvent/photoresist solvent from step b) to C_5–C_8 alkane, water or aromatic solvent, of from about 5:1 to about 0.5:1;

d) rotating the liquid/liquid centrifuge containing the mixtures from step c) at a speed of at least 500 rpm and thereby separating and collecting a two-phase system from 2 separate outlet ports, into two containers, wherein the heavier phase (H) contains the higher molecular weight novolak resin fraction, in the water soluble organic polar solvent and the photoresist solvent with a minor amount of the C_5–C_8 alkane, water or aromatic hydrocarbon solvent, and the lighter phase (L) contains: 1) the lower molecular weight novolak resin fraction, 2) C_5–C_8 alkane, water or aromatic hydrocarbon solvent, 3) water soluble organic polar solvent, and 4) photoresist solvent;

e) as the lighter phase (L) of the two-phase system of step d) is collected, it may separate into two phases, the lighter of these two second phases containing the C_5–C_8 alkane, water or the aromatic hydrocarbon solvent and a minor amount of the water soluble organic polar solvent and about 15-20% of the photoresist solvent, the heavier of these two second phases containing low molecular weight novolak oligomers and unreacted phenolic compounds, dissolved in the water soluble organic polar solvent and the photoresist solvent with about 10-15% of the C_5-C_8 alkane, water or aromatic hydrocarbon;

f) substantially removing the residual C_5-C_8 alkane, water or aromatic hydrocarbon solvent from the heavier phase from step d) and leaving the novolak resin dissolved in the photoresist solvent;

g) providing an admixture of: 1) a photosensitive component in an amount sufficient to photosensitize a photoresist composition; 2) the film forming novolak resin solution from step f); and 3) additional photoresist solvent, if needed, to provide the desired formulation, and thereby forming a photoresist composition.

13. The method of claim 12 wherein said acid catalyst is oxalic acid, maleic acid, maleic anhydride, sulfuric acid, or p-toluene sulphonic acid.

14. The method of claim 12 wherein the water soluble organic polar solvent added in step b) is acetone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, ethylene glycol or a C_1-C_5 alkyl alcohol.

15. The method of claim 12 wherein the photoresist solvent added in step b) is a monooxymonocarboxylic acid ester, a propylene glycol methyl ether acetate, 2-heptanone or a propylene glycol methyl ether, or a mixture of one or more of these.

16. The method claim 12 wherein aromatic hydrocarbon solvent added in step c) is benzene or a C_1–C_5 alkyl benzene.

17. The method of claim 12 wherein the ratio of photoresist solvent to water soluble organic polar solvent added in step b) is from about 10/90 to 70/30.

18. The method of claim 12 wherein the ratio of photoresist solvent to water soluble organic polar solvent added in step b) is from about 30/70 to 60/40.

19. The method of claim 12 wherein the ratio of the mixture from step b) fed into the centifruge to the C_5–C_8 alkane, water or aromatic hydrocarbon solvent fed into the centifruge is from about 2:1 to about 1:0.75.

20. The method of claim 12 wherein the in step b) the materials are fed into the centifruge at a temperature of from about 0°C to a temperature up to about 10°C less than the boiling point of the lower boiling solvent.

21. The method of claim 12 wherein the centifruge is rotated at a speed of from about 500 to 50,000 rpm.

22. The method of claim 12 wherein the centifruge is rotated at a speed of from about 1,000 to 30,000 rpm.

23. A method for producing a semiconductor device by producing a photo-image on a substrate by coating a suitable substrate with a positive working photoresist composition comprising:

a) condensing formaldehyde, para formaldehyde or formalin with one or more phenolic compounds, in the presence of an acid catalyst and thereby producing a novolak resin;

b) adding a water soluble organic polar solvent and a photoresist solvent to the novolak resin reaction mixture from step a), at a ratio of photoresist solvent to water soluble organic polar solvent of from about 10/90 to 70/30;

c) feeding the mixture from step b) into a liquid/liquid centrifuge at a feed rate of from about 0.01 to 100 gallons per minute and at a temperature of from about 0°C up to a maximum temperature that is less than the boiling point of the lower boiling solvent in the mixture from step b0 and feeding a substantially pure C_5–C_8 alkane, water or aromatic hydrocarbon solvent into a separate liquid/liquid centrifuge inlet port at a feed rate of from about 0.01 to 100 gal./min., at a ratio of water soluble organic polar solvent/photoresist solvent from step b) to C_5–C_8 alkane, water or aromatic solvent, of from about 5:1 to about 0.5:1;

d) rotating the liquid/liquid centrifuge containing the mixtures from step c) at a speed of at least 500 rpm and thereby separating and collecting a two-phase system from 2 separate outlet ports, into two containers, wherein the heavier phase (H) contains the higher molecular weight novolak resin fraction, in the water soluble organic polar solvent and the photoresist solvent with a minor amount of the C_5–C_8 alkane, water or aromatic hydrocarbon solvent, and the lighter phase (L) contains: 1) the lower molecular weight novolak resin fraction, 2) C_5–C_8 alkane, water or

aromatic hydrocarbon solvent, 3) water soluble organic polar solvent, and 4) photoresist solvent;

e) as the lighter phase (L) of the two-phase system of step d) is collected, it may separate into two phases, the lighter of these two second phases containing the C_5–C_8 alkane, water or the aromatic hydrocarbon solvent and a minor amount of the water soluble organic polar solvent and about 15-20% of the photoresist solvent, the heavier of these two second phases containing low molecular weight novolak oligomers and unreacted phenolic compounds, dissolved in the water soluble organic polar solvent and the photoresist solvent with about 10-15% of the C_5-C_8 alkane, water or aromatic hydrocarbon;

f) substantially removing the residual C_5-C_8 alkane, water or aromatic hydrocarbon solvent from the heavier phase from step d) and leaving the novolak resin dissolved in the photoresist solvent;

g) providing an admixture of: 1) a photosensitive component in an amount sufficient to photosensitize solvent a photoresist composition, 2) the novolak resin solution from step g);

h) coating a suitable substrate with the photoresist composition of step g);

i) heat treating the coated substrate of step h) until substantially all of the photoresist solvent is removed; image-wise exposing the photosensitive composition and removing the image-wise exposed areas of such composition with a suitable developer.

24. The method of claim 23 wherein the acid catalyst is oxalic acid, maleic acid, maleic anhydride, sulfuric acid, or p-toluene sulphonic acid.

25. The method of claim 23 wherein the water soluble organic polar solvent added in step b) is acetone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, ethylene glycol or a C_1-C_5 alkyl alcohol.

26. The method of claim 23 wherein the photoresist solvent added in step b) is a monooxymonocarboxylic acid ester, a propylene glycol methyl ether acetate, 2-heptanone or a propylene glycol methyl ether, or a mixture of one or more of these.

27. The method claim 23 wherein aromatic hydrocarbon solvent added in step b) is benzene or a C_1–C_5 alkyl benzene.

28. The method of claim 23 wherein the ratio of photoresist solvent to water soluble organic polar solvent added in step b) is from about 10/90 to 70/30.

29. The method of claim 23 wherein the ratio of photoresist solvent to water soluble organic polar solvent added in step b) is from about 30/70 to 60/40.

30. The method of claim 23 wherein the ratio of the mixture from step b) fed into the centifruge to the C_5–C_8 alkane, water or aromatic hydrocarbon solvent fed into the centifruge is from about 2:1 to about 1:0.75.

31. The method of claim 23 wherein in step b) the materials are fed into the centifruge at a temperature of from about 0°C to a temperature up to about 10°C less than the boiling point of the lower boiling solvent.

32. The method of claim 23 wherein the centifruge is rotated at a speed of from about 500 to 50,000 rpm.

33. The method of claim 23 wherein the centifruge is rotated at a speed of from about 1,000 to 30,000 rpm.